

An Efficient Kernel Polynomial Method for Calculating Transition Rates in Large-Scale Materials

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We developed an efficient method for calculating transition rates in large-scale materials. In this method, we first reformulated the prefactor of the transition rate in terms of the density of states (DOS) of the Hessian matrix and then solved for the DOS using the kernel polynomial method. We demonstrated this novel method by calculating the prefactor of the vacancy hop in bulk silver and compared the results to the benchmark that was obtained by directly diagonalizing the Hessian matrix.

The transition rates of important kinetic processes in materials are essential for our understanding and prediction of material properties. For example, the dislocation nucleation rate controls plasticity, which determines how much strain materials can sustain. A recent discovery [1] of a self-healing mechanism shows that grain boundaries after radiation can emit interstitial defects to annihilate the vacancy defects nearby. Such a self-healing mechanism might be relevant for the design of next-generation nuclear reactors. It is then important to know how fast such a self-healing process operates, especially when it is also competing with other processes. However, it is usually too computationally expensive to calculate transition rates in large-scale materials. Within harmonic transition state theory [2], one must calculate all the eigenvalues of the Hessian matrices at the saddle point and the basin minimum. The computational cost then scales cubically with respect to system size. Unfortunately, even a simple atomistic simulation of dislocation nucleation requires thousands of atoms, which in turn produces very large Hessian matrices that can be difficult to diagonalize.

In this work, we present a novel method for calculating transition rates in large-scale materials. To avoid diagonalizing the Hessian matrix, we reformulate the transition rate in terms of the DOS of the Hessian. To efficiently solve for the DOS, we employ the kernel polynomial method (KPM) [3] in which the DOS is expanded with Chebyshev polynomials. The expansion coefficients, that is, the moments, are then obtained with stochastic sampling. In the past, KPM has been successfully applied to the calculation of the DOS in quantum mechanics simulations [4]. To our knowledge, this is the first time the KPM is used in the calculation of transition rates in large-scale materials. Assuming that the required number of moments is constant and assuming short-ranged potentials, our method is linear-scaling with respect to problem size, which makes

it very promising for application to large-scale systems. Our method also offers a good balance between accuracy and computational cost.

We demonstrate our method by computing the rate prefactor for a simple vacancy hop in bulk silver. Tests on more complicated processes are underway. In Fig. 1, we show the saddle point configuration. For simplicity, we show only the atoms around the vacancy, with all bulk atoms removed. Atom A is moving to the vacancy B and creating a new vacancy C. We calculate the prefactor of this transition with KPM and compare it against the benchmark obtained by directly diagonalizing Hessian matrices. In KPM, the zero-th moments are simply equal to the dimensions of the problems; we therefore can fix the zero-th moments to their exact values by properly constructing the random vectors used in the calculation of the moments. In Fig. 2, we show that the convergence of the prefactor with respect to the number of random vectors using exact zero-th moments (red crosses) is much faster than the case without using exact zero-th moments (green circles). In a recent work [5], the prefactor was calculated using thermodynamic integration in which molecular dynamics is performed on model harmonic potentials associated with the saddle point and the basin minimum. Compared to that work, one prominent advantage of our approach is that we can achieve significant error cancellation between the partition functions at the saddle point and the basin minimum by using the same sequence of random vectors for each. In Fig. 2, the blue triangles are calculated using two different sequences of random vectors and converge much slower than the case with matched random vectors. In the lower plot of Fig. 2, we show an even slower convergence using inexact zero-th moments and non-matched random vectors. In Fig. 3, we show the convergence speed of the prefactor with respect to the number of moments. The prefactors converge to better than 10% error with less than ten moments. Such fast convergence makes our method very appealing. In Fig. 4, we show the convergence of prefactors with respect to random vectors for five

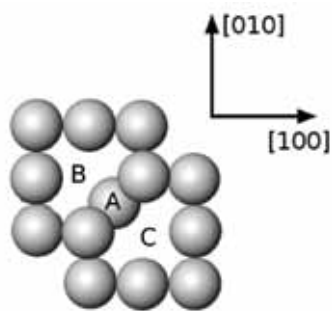


Fig. 1. Saddle point configuration for vacancy hopping. Atom A is moving to vacancy B and creating a new vacancy C. For simplicity, we performed the common neighbor analysis and removed all atoms in face-centered cubic environment.

different cell sizes. The 10% errors are drawn with dashed lines. For all cell sizes, the prefactors converge to the $\pm 10\%$ window with fewer than 3,000 random vectors.

In summary, we have developed a powerful method for calculating transition rates of important processes in large-scale materials. Great insight should be accessible with this method, for processes such as the migration speed of dislocations in metals under shock-waves, which controls the flow of plasticity, the unexpected short lifetime of dislocations in metal nanocrystals, which is responsible for their ultra-strength, and the aggregation of small voids to form large voids under stress, which causes the failure of materials.

Fig. 2. Comparison of the convergence speeds of prefactors (using 400 moments) with respect to the number of random vectors for four different schemes. (Upper plot) We show results from (1) exact zero-th moments and matched random vectors (red crosses), (2) exact zero-th moments and non-matched random vectors (blue triangles), and (3) inexact zero-th moments and matched random vectors (green circles). (Lower plot) Results from inexact zero-th moments and non-matched random vectors. The fluctuation is much larger than the other cases. Exact prefactors are shown by dashed lines in both plots.

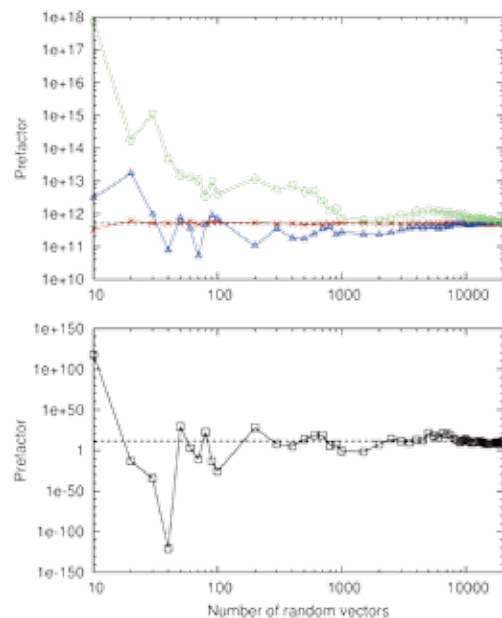


Fig. 3. Convergence of prefactors (using 20,000 random vectors) with respect to the number of moments in the Chebyshev expansion, for five different cell sizes. We find a very fast convergence of prefactors by increasing the number of moments. With 10, 20, 30, 40, and 50 moments, prefactors converge to 8%, 4%, 2%, 0.8%, and 0.6%, respectively.

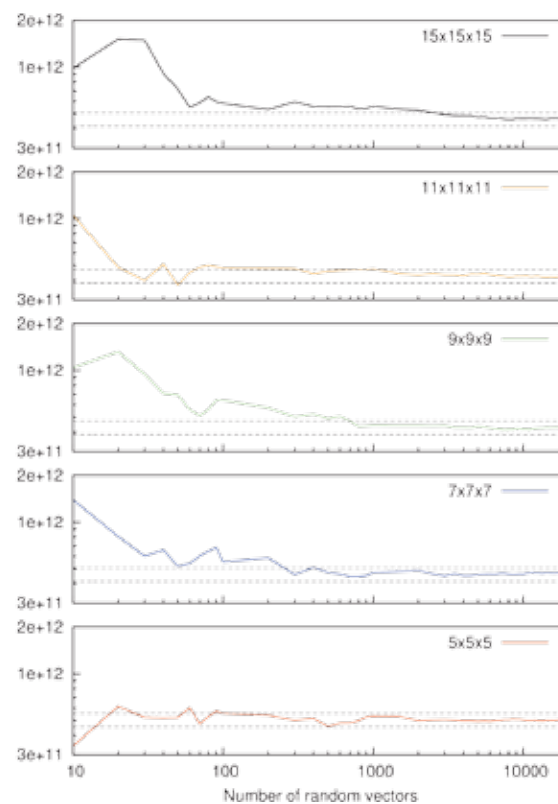
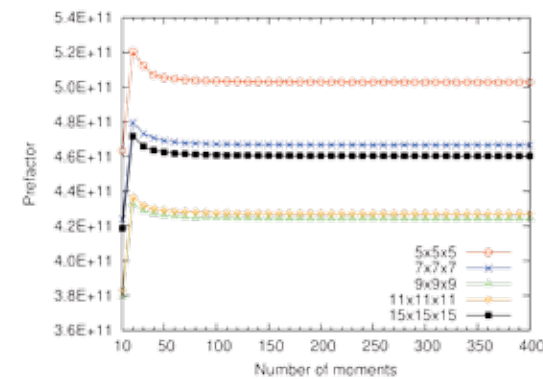


Fig. 4. Convergence of prefactors (using 400 moments) with respect to the number of random vectors, for five different cell sizes. The dashed horizontal lines show the $\pm 10\%$ errors from the benchmark which is calculated by directly diagonalizing the Hessian matrices (except for the 15x15x15 cell, where the benchmark is taken from the converged KPM result at 20,000 random vectors).

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